Association of Metallurgical Engineers Serbia and Montenegro Scientific paper AME UDC:669.715.017.2:620.192.4=20

MICROSTRUCTURAL CHARACTERIZATION OF MODIFIED COMMERCIAL 2219 ALUMINUM ALLOY

V. MAKSIMOVIĆ¹, Z. CVIJOVIĆ² and V. RADMILOVIĆ³

¹Institute of Nuclear Sciences, "Vinča", 11001 Belgrade, Serbia and Montenegro, vesnam@vin.bg.ac.yu, ²Faculty of Technology and Metallurgy, University of Belgrade, 11120 Belgrade, Karnegijeva 4, Serbia and Montenegro, ³National Center for Electron Microscopy, LBLN, University of California, Berkeley, USA

ABSTRACT

The microstructural analysis of a commercial 2219 alloy modified with a small (Si+Ge) addition was carried out using different analytical techniques. The intermetallic phases characteristic for alloy in the as-cast and artificially aged conditions were determined. The presence of $CuAl_2$ phase, which cannot be dissolved during solution treatment and various phases containing Cu, Mn, Fe and Si in overaged microstructure indicates that more Cu was removed from the solid solution and did not contribute to hardening. This clearly demonstrates that the beneficial effect of Si and Ge on the age-hardening response is controlled by the actual composition of matrix.

Key words: commercial 2219 aluminum alloy, (Si+Ge) addition, microstructural state, intermetallic phases, characterization of microstructure

INTRODUCTION

The 2000 series wrought Al-Cu alloys are widely used as high-strength structural alloys. Despite their high strengthening potential, there is a research interest for the effects of microalloying with Si and Ge on the age-hardening response of these alloys [1,2]. Namely, the observation that the experimental Al-Si-Ge-Cu alloys display very fast aging response, high peak hardness and better microstructural stability after prolonged aging [3,4] indicates that combined additions of Si and Ge may be used to produce higher precipitation hardening than that which occurs in the commercial 2000 alloys. The precipitation of densely distributed Si-Ge particles prior to the θ' metastable phase formation [1-6] results in a significantly higher peak hardness achieved at a shorter aging time [2].

However, the commercial Al alloys normally contain the Mn, Ti, Zr, V, Fe and Si as impurities or additional alloying elements, which induce formation of the secondphase particles. Thus, due to its extremely low solid solubility in Al, nearly all Fe segregates to dendrite arm boundaries during solidification where it reacts with Al, Si, Cu and Mn to form a large number of intermetallic phases. As these particles are insoluble and may only undergo phase transformation during ingot homogenization, Cu does not have the same potential to influence precipitation behavior of the alloys. On the other hand, increasing the concentration of Si through microalloying leads to the formation of phases, which are distinguished by their higher Si contents. They can reduce a subsequent precipitation of Si-Ge particles, which act as heterogeneous sites for nucleation of Cu based metastable phases during aging [1,2]. Since the chemical composition and local cooling rate are factors that determine the solidification paths and which phases will form [7], it is important that the microstructure of modified 2000 alloys be fully defined.

The present study was undertaken to determine the intermetallic phases that might form during casting and heat treatment in a commercial 2219 alloy modified by the simultaneous additions of Si and Ge.

EXPERIMENTAL

The investigated alloy with the chemical composition in mass % 5.9Cu-0.69Ge-0.28Si-0.26Fe-0.29Mn-0.01Mg-0.06Zn-0.08Ti-0.13Zr-0.09V-0.007Cr-bal. Al was prepared by adding master alloys Al-12% Si and Al-50% Ge to the base 2219 alloy (the chemical composition is given in mass% if other vice not stated). The molten metal was poured into a graphite crucible to obtain small ingot. After machining, ingot was homogenized for 48 h at 500°C and hot-rolled from 27 mm to 2 mm in thickness. A sheet was subsequently subjected to annealing for 24 h at 500°C, water quenching, holding at room temperature for 9 days, and then aged at 190°C for 150 h.

The microstructure of alloy in as-cast and overaged conditions was examined using optical microscopy (OM), JEOL JSM-5300 scanning electron microscope (SEM) and JEOL 200CX transmission electron microscope (TEM). The phase identifications were carried out by selective etching and energy dispersive spectroscopy (EDS). The volume fraction of coarse intermetallic particles was determined by image analysis.

RESULTS AND DISCUSSION

The examination of as-cast microstructure shown in Fig.1 indicated that it consists of several intermetallic phases with different morphologies, in addition to the Al matrix. These are well-defined CuAl₂ eutectic network (E) with traces of light gray particles (P) growing at its edges, dark gray platelets (PL) and gray needles (N) co-existing with the eutectic phase, signifying the end of solidification.

Among all the present phases, the CuAl₂ phase dominates. This identification was verified by EDS in the SEM mode. Although the composition varied from particle to particle, they contain mainly Al and Cu. The composition of this phase is listed in Table 1. Based on this identification, the image analysis show that after casting the microstructure contains 6.8 vol. % of CuAl₂ phase. This, in turn, would lead to a low Cu content in the matrix. As can be seen from Table 1, Cu builds up to 1.42% in the matrix, a value much lower than the normal content of Cu in the alloy. At the same time, the Fe content reached its solubility limit in Al, which is 0.05%. Thus, the amount of Fe available to form intermetallics is 0.21%. The entrapped Si content in the matrix is even lower than that of Fe, due to the high diffusion coefficient of Si in Al. This would explain the formation of Fe- and Si-containing intermetallic particles in considerable amount of 1.35 vol. %.





Fig.1. Optical micrographs showing as-cast microstructure of modified 2219 alloy.

Namely, the solidification started with the development of the Al dendritic network. As solidification proceeded, the liquid phase was enriched with Fe and Si from which the Fe- and Si-containing phases could precipitate. The EDS results showed that dark gray platelets (PL), observed more frequently than gray needles (N), contain mainly Al, Cu and Fe. These particles were, therefore, identified as the Cu₂FeAl₇ phase. Their average composition listed in Table 1 shows a deviation from the stoichiometry of the Cu₂FeAl₇ phase. However, particles coexisting with the eutectic CuAl₂ phase and invariant reaction liq. \rightarrow Al + Cu₂FeAl₇ + CuAl₂ + Si + AlFeMnSi occurring in Al-Cu-Fe-Mn-Si system [7] indicate that this phase may be present. The phase listed as AlFeMnSi is probably Al₁₅(Fe,Mn)₃Si₂ with some Cu in solution. That the preceding reaction can take place during solidification suggests the appearance of small particles (light gray) attached to the sides of the eutectic CuAl₂ phase. Due to their sparse occurrence in the microstructure, detailed characterization of these particles was not performed. Since the Mn content in the matrix decreased to 0.17%, it could be assumed that Fe reacts with the Al, Si and Mn leading to the formation of the AlFeMnSi phase.

Phase	Elements, mass %						Dhase
Number	Al	Cu	Fe	Si	Ge	Mn	1 hase
1	98.10	1.42	0.05	_*	0.27	0.17	Matrix
2	82.77	17.23	-	-	-	-	CuAl ₂
3	52.70	45.31	1.91	-	-	-	Cu ₂ FeAl ₇
4	34.16	34.14	0.77	31.93	-	-	Al ₅ FeSi

Table 1. EDS analysis of phases observed in as-cast microstructure of modified 2219 alloy

*Traces

Addition of an excessive amount of Si to the 2219 alloy results in the precipitation of the intermetallic phase in the form of thin needles (N), gray in color. From considerations of the morphology and EDS analysis, the composition of this phase in Fig. 1a was estimated as being Al₅FeSi. Since Fe reacts either with Al and Cu to form Cu_2FeAl_7 phase or with Al, Mn and Si to form AlFeMnSi phase, most of the Si will

combine with Al and remaining Fe to precipitate as Al_3FeSi . Also, when the Fe/Si ratio is < 1, which corresponds exactly to our case, Si tends to stabilize the Al_3FeSi phase needles in the as-cast microstructure. Substitution of Al and Fe with some amount of Cu might lower the temperature of the complex eutectic reaction corresponding to the formation of the Al_3FeSi phase, so that solidification ended with this reaction. It is obvious that the formation of $(Al,Cu)_5(Fe,Cu)Si$ phase, containing higher Si level than the matrix, may cause a relatively small amount of Si available to combine with Ge to form Si-Ge particles during subsequent heat treatment. In contrast, all the Ge is present within the matrix.

During termomechanical and heat treatment of the cast alloy, the intermetallic particles may undergo changes stimulated by chemical and surface energy driving forces. Figs. 2 and 3 represent the overaged microstructure and EDS spectra obtained from the most often observed particles.



Fig.2. TEM micrograph of particles in overaged microstructure with corresponding EDS spectra.

As shown in Fig.2, $CuAl_2$ particles are still present after aging for 150 h at 190°C. The metastable $CuAl_2$ phase was partially dissolved, providing the higher Cu content in the matrix. According to the X-ray diffraction data reported earlier [2] the Cu concentration in supersaturated matrix of as-quenched microstructure increases to 4.30%, resulting in a larger driving force for precipitation during aging. However, as dissolution of $CuAl_2$ phase proceeded slowly, the volume fraction of its undissolved particles remained after annealing at 500°C is relatively high (1.82 vol. %). They are

usually round shaped and in the form of isolated individual particles, due to their fragmentation and spheroidization. The particles of Cu_2FeAl_7 phase are another type of particles frequently found in overaged microstructure, Fig. 2. There is practically no effect on the dissolution of this phase.



On the other hand, most of the (Al,Cu)₅(Fe,Cu)Si particles were disappeared from the microstructure. This is coupled with the rejection of Si out of the particles and their decomposition, resulting in the progress of Al₁₅(Fe,Mn,Cu)₃Si₂ formation. This observation is supported by the relatively larger amount of all Fe- and Si-containing intermetallic particles. Their volume fraction in as-quenched microstructure is 1.43 vol. %. Although the hot rolling causes significant fragmentation of all phases existing in the as-cast condition, the fragmentation of (Al,Cu)₅(Fe,Cu)Si particles enhances their dissolution in the matrix, while decomposition of the Al₁₅(Fe,Mn,Cu)₃Si₂ particles was not observed even after 24 h at 500°C. The bright field TEM image of the overaged microstructure (Fig. 3a) reveals the presence of fine polyhedral particles of this phase. The EDS spectrum (Fig. 3b) taken from this particle (marked A in Fig. 3a) displays reflections due to Al, Si, Mn, Fe and Cu elements. Their respective atomic concentrations were found to be 73.07, 10.47, 10.81, 3.73 and 1.56 %, giving it a chemical composition of $Al_{13.96}(Fe,Mn,Cu)_{3.07}Si_2$, which is very close to $Al_{15}(Fe,Mn,Cu)_3Si_2$.

The dissolution of $(Al,Cu)_5$ (Fe,Cu)Si particles may contribute to the higher level of Si content entrapped in the supersaturated matrix of as-quenched microstructure, enhancing the precipitation of the Si-Ge particles during subsequent aging. Figure 3a demonstrates that these particles are present in a relatively high amount. Figure 3c is the EDS spectrum obtained from the particle marked C in Fig. 3a. It confirmed that they contain only Si and Ge. That the pre-existence of Si-Ge particles may promote precipitation of θ' metastable phase is revealed by the EDS analysis of particles such as those marked B in Fig. 3a. As expected, the obtained EDS spectrum exhibits reflections due to Al, Cu, Si and Ge, indicating that the θ' precipitates grow around the Si-Ge particles.

CONCLUSIONS

The characterization of as-cast and heat treated microstructure in a commercial 2219 alloy modified with small addition of (Si+Ge) showed that the coarse intermetallic particles, which were formed during casting, play an important role in determining the age-hardening response of this alloy. Their presence attributed to the complex chemistry of the commercial alloy system reduces the Cu potential and precipitation of Si-Ge particles which are responsible for the strengthening effect. The formation of CuAl₂, Cu₂FeAl₇, Al₁₅(Fe,Mn,Cu)₃Si₂ and (Al,Cu)₅(Fe,Cu)Si phases in the total amount of 8.22 vol. % decreases significantly the Cu and Si concentrations in the matrix available to precipitate as Si-Ge particles or metastable θ' phase. During solution heat treatment, the CuAl₂ phase partially was dissolved while the (Al,Cu)₅(Fe,Cu)Si decomposed into Al₁₅(Fe,Mn,Cu)₃Si₂ and Si, contributing to the supersaturation of matrix. In contrast, both Cu₂FeAl₇ and Al₁₅(Fe,Mn,Cu)₃Si₂ are stable at 500°C. This limits the Cu and Si levels in the matrix and, thereby, the beneficial effect of Si and Ge additions.

ACKNOWLEDGEMENT

Authors are indebted to the Ministry of Science and Environmental Protection of the Republic of Serbia for the financial support through the project No.1261.

REFERENCES

- V. Maksimović, A. Tolley, M.T. Jovanović, V. Radmilović, Mater. Sci. Forum, 453-454 (2004) 323.
- [2] V. Maksimović, Master's thesis, University of Belgrade, Belgrade, Serbia and Montenegro, 2003.
- [3] D. Mitlin, V. Radmilović, U. Dahmen, Metall. Mater. Trans. A, 32A (2001) 197.
- [4] D. Mitlin, V. Radmilović, J.W. Morris Jr., U. Dahmen, Metall. Mater. Trans. A, 34A (2003) 735.
- [5] V. Radmilović, D. Mitlin, A.S. Tolley, U. Dahmen, J.W. Morris Jr., Metall. Mater. Trans. A, 34A (2003) 543.
- [6] A.K. Mukhopadhyay, Metall. Mater. Trans. A, 32A (2001) 1949.
- [7] L.F. Mondolfo, Aluminum Alloys, Structure and Properties, Butterworths, London, 1976.